

- (21) Application No. 14429/78 (22) Filed 12 Apr. 1978 (19)  
(31) Convention Application No. 792350 (32) Filed 29 Apr. 1977 in  
(33) United States of America (US)  
(44) Complete Specification Published 2 Apr. 1980  
(51) INT. CL.<sup>3</sup> C08K 9/04  
(52) Index at Acceptance  
C3K 124 241 293 400 GG  
C3W 221 223  
C3Y B180 B184 F110



(54) CaCO<sub>3</sub> FILLED SIDING WITH IMPROVED WEATHERING

(71) We, GAF CORPORATION, a corporation organized and existing under the laws of the State of Delaware, United States of America, having its main office at 140 West 51st Street, New York, New York 10020, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

Calcium carbonate is a commonly used filler for rigid polyvinyl chloride (PVC) compounds used in making various products such as pipes. While not commonly used, calcium carbonate has also been used as a filler in PVC siding.

PVC products intended for exterior use require protection for ultraviolet (UV) radiation to avoid excessive fading and chalking. While some products are made with a separate outer layer or protected coating adapted to provide such protection, it is frequently desired to provide such protection against weathering by incorporating one or more UV absorbers in the PVC composition itself.

Unfortunately UV stabilized, white PVC products such as those used for building panels are subject to some yellowing of the product; particularly during the initial stages of exposure. Such yellowing can be reduced by incorporating additional amounts of UV absorber. UV absorbers are, however, expensive and it is desirable to use a minimum amount of UV absorber consistent with desired resistance to weathering.

It is an object of the invention to provide improved synthetic resin composition suitable for making white, rigid products such as building panels.

It has now been found that calcium carbonate may be used successfully as a filler in white PVC or related resin compositions, including building panels such as siding, provided finely ground amorphous calcium carbonate is used and the individual particles of calcium carbonate are coated with a calcium salt of a higher fatty acid. More specifically, the invention provides a white synthetic resin composition comprising:

a) a synthetic resin which is or contains a polymer or copolymer of vinyl chloride or vinylidene chloride, with vinyl chloride or vinylidene chloride residues being the predominant constituent of the resin.

b) between 2 and 50 pounds per hundred pounds of resin (PHR) of finely divided amorphous calcium carbonate filler having an average particle size between 0.1 and 1.0 micron with at least 90% of such calcium carbonate particles used having a maximum particle size of not more than 2 microns, the individual particles of such filler being coated with the calcium salt of a higher fatty acid of at least 12 carbon atoms; and

c) an effective amount of a UV absorber.

In a preferred embodiment, the higher fatty acid is stearic acid so that the resulting calcium carbonate filler particles are coated with calcium stearate. Preferred embodiments also include the use of TiO<sub>2</sub> as both a pigment and as a UV absorber. The invention also embraces rigid building panels such as PVC siding comprising the composition of the invention.

As mentioned above, the composition of the invention comprises PVC or related synthetic resin finely divided amorphous calcium carbonate coated with the calcium salt of a higher fatty acid and a UV absorber.

Synthetic resin suitable for use in compositions and rigid building panels of the invention includes any of the conventional PVC materials generally considered suitable for use in the manufacture of rigid PVC products. These include, for instance, materials such as polyvinyl

chloride itself, poly vinylidene chloride, copolymers thereof, post chlorinated polyvinyl chlorides, mixtures of polyvinyl chlorides with chlorinated polyethylenes or acrylonitrile, butadiene/styrene copolymers, etc. PVC material for use in the invention usually has a weight average molecular weight between 30,000 and 200,000 more usually between 50,000 and 100,000.

It is generally preferred that the synthetic resin used in the products of the invention be at least 80 wt% vinyl chloride polymer with from 0 to 20 wt% of one or more of the other monomers of copolymers mentioned being present.

Suitable coated calcium carbonate filler is based upon finely divided amorphous calcium carbonate such as chalk. The use of more crystalline forms of calcium carbonate such as marble does not appear to provide the unexpected advantages found when coated particles of amorphous calcium carbonate are used. Finely ground amorphous calcium carbonate having an average particle diameter between 0.1 and 1.0 microns with a maximum particle size for at least 90% of the particles of not more than 2 microns is required.

The individual particles of amorphous calcium carbonate are coated with the calcium salt of a higher fatty acid, i.e., a fatty acid having at least 12 carbon atoms in the molecule. Stearic acid is a preferred fatty acid for use in preparing the product of the invention. The calcium salt coating may be obtained in a conventional manner by mixing the fatty acid with the calcium carbonate particles, preferably at temperatures between 60 and 200°C so that the fatty acid reacts with the surface of the calcium carbonate to form on the carbonate particles an adherent coating of calcium salt. Such coating substantially covers the individual particles, although it should be understood that in some instances some of the fatty acid may also be present on the surface of the carbonate particles. Coated calcium carbonate filler used in products of the invention is well known for other uses such as in the manufacture of PVC products which do not contain UV absorbers. Such filler is available, for instance, under the trade name Omyalite 90T. Coated calcium carbonate filler as described herein is used in products of the invention in amounts ranging between 2 and 50 PHR. For exterior applications such as siding, where weatherability is a problem, amounts between 5 and 35 PHR, more especially between 5 and 12 PHR are preferred.

It is preferred that the total of calcium salt of higher fatty acid present as coating on the calcium carbonate particles and any unreacted higher fatty acid be present in products of the invention in amounts not exceeding 3 PHR. Excessive amounts of higher fatty acid or salts thereof can result in overlubrication, whereby impact strength and homogeneity of the finished product is adversely affected.

As mentioned above, PVC products such as siding, intended for exterior use require the incorporation of UV absorbers in the PVC composition if excessive fading or chalking due to weathering is to be avoided. UV absorbers may be any of the materials commonly sold for such purpose, including for instance benzotriazoles benzophenones and substituted acrylonitriles. Alternatively, additional  $\text{TiO}_2$  may be incorporated into the composition so that the  $\text{TiO}_2$  functions as a UV absorber as well as a white pigment.  $\text{TiO}_2$  when used as a pigment is normally used in amounts between 1 and 3 PHR. When additional  $\text{TiO}_2$  is incorporated for the purpose of providing UV protection as well as normal pigmentation, the amount of  $\text{TiO}_2$  used is normally between 5 and 25 PHR. Other UV absorbers, when used, are normally used in amounts between 0.1 and 5 PHR.

The titanium dioxide used as a pigment or as a UV absorber in the products of the invention may be any titanium dioxide normally used as white pigmentation in rigid PVC products. The rutile form of  $\text{TiO}_2$  is considered most satisfactory since its relatively higher refractive index and reflectivity and opacity is desirable. However, for economy it is possible to use up to 40 wt% based on  $\text{TiO}_2$  of the anatase form. Excessive amounts of anatase are undesirable because of the recognised inferiority of anatase relative to rutile in regard to weathering characteristics of the finished product. This is especially significant in the production of building panels, such as siding, intended for exterior use.

In addition to the basic ingredients of synthetic resin, calcium carbonate particles and  $\text{TiO}_2$ , described above, the products of the invention may contain other ingredients normally used in rigid PVC products such as stabilizers, processing aids, lubricants, impact modifiers, additional fillers, etc. Such other ingredients, when used, frequently are used in amounts totaling between 10 and 40 PHR. Conventional plasticizers such as dioctyl phthalate, dihexyl phthalate, phthalate esters, etc. may also be included in the products of the invention. Depending on the particular physical properties desired, other ingredients used, etc., plasticizer may be included in compositions of the invention in amounts up to 30 PHR.

Rigid compositions of the invention may be manufactured in any suitable conventional manner, such as by powder or pellet extrusion, calendering, thermoforming, etc., it being understood that suitable methods for manufacturing rigid products such as pipes, siding, etc. are well known in the art and do not constitute a part of this invention. While manufacturing methods are not a part of the invention, it should also be understood that the

particular manufacturing technique selected may effect the desirable formulation of the product of the invention within the broad limits given above.

The following examples illustrate preferred embodiments and advantages of the invention, but are not intended to limit the scope of the invention. In examples, yellowing of the various samples tested was measured after six months exposure. This particular time interval was selected because white PVC siding pigmented with  $\text{TiO}_2$  characteristically yellows to the maximum degree in about this time at the location where these tests were carried out. Following initial yellowing, chalking usually occurs followed by further yellowing. The yellowing is normally at its worst, i.e. most yellow, about 3-9 months after initial exposure depending upon the climatic conditions to which the siding is exposed.

#### Example 1

To evaluate the effectiveness of various forms of calcium carbonate filler in reducing yellowing of white PVC siding, a number of siding samples were prepared from filled compounds formulated as described herein and exposed in a southerly direction at an angle of about  $45^\circ$  in northern NEW Jersey for a period of six months. The various calcium carbonate filled PVC compounds from which the siding panels tested were produced were formulated and extruded in a conventional manner using screw extruders and the siding panels were produced by conventional extrusion techniques. The method of manufacture was in all cases substantially identical. The only difference in the various panels tested was the type of calcium carbonate filler used. For these tests the formulation used comprised, in addition to the calcium carbonate filler, the following ingredients:

<i>Ingredient</i>	<i>Parts by Weight</i>
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25	PVC Homopolymer (I.V. 0.09)	100	25
	Tin Stabilizer	1.6	
	Acrylic Impact Modifier	7.0	
	Process Aid	1.5	
	Wax	0.95	
30	Calcium Stearate	2.00	30
	$\text{TiO}_2$ (semi-rutile)	14.00	

Calcium carbonate particles were in each instance used in the formulation tested in an amount of 10 PHR. Calcium carbonate particles used in forming siding samples A-F, for which test results are reported below, were as follows:

Sample A was a control sample in which no calcium carbonate filler was used.

Sample B used calcium carbonate particles wet ground to an average particle size of 2.5 microns from amorphous chalk with the maximum particle size being about 10 microns (i.e. at least 90% of the particles were no larger than 10 microns in size). These calcium carbonate particles were coated with calcium stearate.

Sample C incorporated calcium carbonate particles obtained by wet grinding marble to an average particle size of 0.7 microns with a maximum particle size of 2 microns. These particles also were coated with calcium stearate.

Sample D incorporated amorphous calcium carbonate particles wet ground to an average particle size of 0.7 microns with a maximum particle size of about 2 microns. These particles were coated with calcium stearate.

Sample E incorporated calcium carbonate particles ground from a relatively crystalline calcium carbonate to an average particle size of 0.7 microns with a maximum particle diameter of about 2 microns. These particles were not coated with calcium stearate.

Sample F incorporated calcium carbonate particles formed by precipitation and having particle size diameters between 0.1 and 0.35 micron. These particles were not coated with calcium stearate.

Table I below shows the results obtained when the samples of siding described above were first exposed immediately after manufacture and after six months' exposure under the conditions described above. In Table I, values are reported for both "Hunter Color L" (a conventional test in which the L value measures lightness with an L value of 100 being perfectly white) and the "b" value (another conventional test in which the b value indicates degree of yellowing with increasing yellowing causing positive changes in b value).

*TABLE I*  
*Effect of Various Calcium Carbonates on Whiteness Retention*

	Sample A (Control)		Sample B		Sample C		Sample D		Sample E		Sample F	
	L	b	L	b	L	b	L	b	L	b	L	b
Initial Exposure	96.9	0.9	91.6	0.4	92.6	0	92.5	0.5	92.7	-0.1	94.7	0.3
After 6 months Exposure	96.6	1.6	92.4	1.0	92.2	0.8	92.8	0.6	92.4	0.8	94.4	0.9
Difference	0.3	0.7	0.8	0.6	0.4	0.8	0.3	0.1	0.3	0.9	0.3	0.6

From Table I it can be seen that the control sample A containing no calcium carbonate filler has a delta b (representing the difference between the b value measured immediately after manufacture and that measured after six months' exposure) of 0.7. By contrast sample D, the only sample tested which was formulated in accordance with the invention, had a delta b after six months' of only 0.1. Other samples tested, none of which were formulated in accordance with the invention, had delta b values after six months ranging from 0.6 to 0.9. It is thus apparent that both the uncoated calcium carbonate filler and the coated calcium carbonate filler in which crystalline calcium carbonate was used were of essentially no help in improving the yellowing characteristics of the finished siding. Even the coated amorphous calcium carbonate having an average particle size of 2.5 microns (sample B) was unsatisfactory in this respect. Only the siding sample formulated in accordance with the invention, i.e., containing very fine ground amorphous calcium carbonate particles coated with calcium stearate, provided this unexpected advantage.

#### *Example II*

This example illustrates the effectiveness of the finely divided amorphous calcium carbonate filler required by the invention in reducing yellowing of white PVC siding exposed in a southerly direction at an angle of about 45 degrees in Arizona for a period of nine months. The siding panels tested were produced in the same manner described above in Example I. The control sample was produced from the same formulation used in producing the control Sample A of Example I, while the remaining samples tested in this example were produced using various amounts of the same coated calcium carbonate particles utilized in Sample D of Example I. The composition of the sample tested in this example and changes in b values of the samples tested after six and nine months are reported in Table II below.

TABLE II

Sample	Amount Coated $\text{CaCO}_3$ (PHR)	Difference in b Value after 6 mo.	Difference in b Value after 9 mo.
G	0	7.5	5.0
H	6	3.0	1.0
I	9	4.0	2.0
J	12	3.0	1.0

It can be seen that Examples H, I and J which contain varying amounts of coated calcium carbonate filler according to the invention exhibit substantially less difference in b values than did the control G which did not contain the coated calcium carbonate filler. The substantially larger differences in b value in Example II versus those reported in Example I were due to the fact that the test panels for Example II were exposed in Arizona rather than New Jersey and were therefore subjected to considerably greater amounts of solar radiation.

### Example III

This example demonstrates the usefulness of the invention when chlorinated polyethylene (CPE) impact modifier is used. Such impact modifier is known to cause yellowing of PVC products to the extent that more expensive acrylic impact modifiers have in the past normally been used for PVC products intended for exterior use. As shown in the example, white PVC products of the invention may include ingredients such as CPE which normally promote yellowness upon prolonged exposure of the product to the sun. For this evaluation four compounds identified below as compounds K, L, M & N were tested according to the procedure outlined in Example I. Compounds K and M had the following compositions.

20	Ingredient	Compound K (PHR)	Compound M (PHR)	20
	PVC Homopolymer (0.9 I.V.)	100	100	
25	Tin Stabilizer	1.6	1.6	25
	CPE	10.0	15.0	
30	Process Aids	1.5	1.5	30
	Calcium Stearate	2.0	2.0	
35	Wax	0.95	0.95	35
	TiO <sub>2</sub>	7.0	7.0	

Compound L was identical with compound K except for the addition of 20 PHR of the coated calcium carbonate of Sample D of Example I and compound N was identical with compound M except for the addition of 35 PHR of the coated calcium carbonate of Sample D of Example I. When formed into test panels and evaluated for changes in b value according to procedures outlined in Example I, the following results were obtained.

45	Sample:	K	L	M	N	45
	Difference in value after 6 mos. exposure	2.2	1.11	2.58	1.24	

### WHAT WE CLAIM IS:-

1. White synthetic resin composition comprising:
  - a) a synthetic resin which is or contains a polymer or copolymer of vinyl chloride or vinylidene chloride, with vinyl chloride or vinylidene chloride residues being the predominant constituent of the resin;
  - b) between 2 and 50 PHR of finely divided amorphous calcium carbonate filler having an average particle size between 0.1 and 1.0 micron with at least 90% of such calcium carbonate particles used having a maximum size of not more than 2 microns, individual particles of such filler being coated with the calcium salt of a higher fatty acid of at least 12 carbon atoms; and
  - c) an effective amount of a UV absorber.
2. A composition according to claim 1 wherein the UV absorber is present in amounts between 0.1 and 5 PHR and TiO<sub>2</sub> is present as a pigment in amounts between 1 and 3 PHR.
3. A composition according to claim 1 wherein TiO<sub>2</sub> is present as pigment and as a UV absorber and is present in a total amount between 5 and 25 PHR.
4. A composition according to any of claims 1 - 3 wherein the calcium carbonate filler is

present in amounts between 5 and 35 PHR.

5. A composition according to any of claims 1 - 4 wherein the calcium salt of a higher fatty acid is calcium stearate.

6. A composition according to any of Claims 1-5 wherein the  $\text{TiO}_2$  is rutile containing between 0 and 40% anatase.

7. A white PVC composition substantially as any of samples D, H, I, J, L or M exemplified herein.

8. A rigid plastic building panel comprising the composition of any of Claims 1-7.

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Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1980.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
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